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Steam Stripping and Batch Distillation for the Removal/Recovery of Volatile Organic Compounds

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in Rosemont, Illinois, on March 16, 1989

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Abstract

Steam stripping and batch distillation are two techniques under investigation by the Hazardous Waste Treatment Branch of the US EPA Risk Reduction Engineering Laboratory. The purpose of these studies is to evaluate the application of these methods to aqueous and dilute organic solutions which are currently subject to land disposal restrictions. General design equations which can be used to assess the applicability of steam stripping to achieve a given separation are included. Preliminary results of a pilot-scale steam stripping study with 2-nitropropane are reviewed. General design procedures for batch distillation are also discussed.

Introduction

As a result of the 1984 Hazardous and Solid Waste Ammendments (HSWA) of the Resource Conservation Recovery Act, US EPA has been directed to develop technology based standards for treatment and disposal of hazardous wastes that are currently undergoing land disposal. The Hazardous Waste Treatment Branch of the US EPA Risk Reduction Engineering Laboratory in Cincinnati has been carrying out a treatment technology assessment program at its Test and Evaluation Facility. Included in this work is the treatment of aqueous and dilute organic solutions through pilot-scale physical separations. At present, steam stripping and batch distillation are in different phases of shakedown and testing at the Test and Evaluation Facility.

Steam Stripping

Steam stripping has been widely used to remove volatile organic chemicals from aqueous solutions. A packed or tray tower separates a contaminated feed into a treated effluent or bottoms and a more concentrated organic overheads stream. This separation is accomplished by directly injecting steam into the column. In the common countercurrent mode of operation, the feed is introduced at or near the top of the column while steam enters at the bottom. Through the use of trays or packing, the steam is brought into intimate contact with the feed. Volatile organics migrate into the vapor phase and exit through the top of the tower. A condenser is used to recover the stripped organics which are then commonly sent to a decanter. Inside the decanter, the heterogeneous overheads separates into aqueous and organic rich phases, with the aqueous phase commonly returned as reflux.

Environmental applications of steam stripping frequently require a unique perspective on the part of the designer. Stripping can be used for solvent recovery, in which case the purity of the overheads is of primary interest. However, it can also be used to meet certain effluent requirements. A stripping column which tries to simultaneously meet both goals will require additional theoretical stages. Great care must also be exercised in the design of the condenser and handling of the vent gases. Otherwise the water treatment or solvent recovery operations may produce unacceptable air emissions. A well designed stripper, with the appropriate auxillary equipment and post-treatment options, can be applied in a number of areas. These include groundwater treatment, treatment of solvent containing rinsewater, and solvent recovery. Steam stripping can successfully handle higher concentrations and less volatile organics than air stripping. For high levels of contamination, distillation becomes more cost effective. These wastes may only be stripped after some form of pretreatment (options include chemical oxidation, precipitation, centrifugation, membrane separation, and flotation).

Steam stripping is most applicable to the removal of a)small amounts of impurities in large

volumes of water, b)components which form low boiling azeotropes with water, c)compounds which are thermally unstable or reactive at high temperatures, d)compounds which cause excessive fouling, and e)in cases where direct fired heaters are ignition or explosion hazards. Halogenated and aromatic compounds are especially suited. Breton, et. al. (1986) suggested a boiling point less than 150°C and a Henry's Law constant greater than 10^{-4}atm-m^3/mol as criteria for steam stripping suitability. Cases where the solubility is greater than 1000 ppm, the boiling point in excess of 150°C, the volatile organic carbon (VOC) content greater than 10%, and the concentration of suspended solids higher than 2% are usually poor candidates.

The bottoms from steam strippers may be suitable for discharge to POTW, or require polishing by biological treatment or activated carbon. If nonvolatile sludges or oily wastes are present, Breton et. al. (1986) suggest decanting or centrifuging the bottoms. When the overheads is to be recovered, drying, selective adsorption, or fractional distillation may be necessary. For solvent recovery operations it should be noted that if a low boiling azeotrope occurs, the maximum overheads concentration will be the azeotrope composition. High concentration in the overheads can be achieved through the use of reflux and rectification. By returning a portion of the condensed vapor to the top of the tower as reflux, higher concentrations of organics in the vapor phase may be obtained. A similar effect occurs when the feed is introduced at a lower tray. If feed is introduced at the top of the column without reflux, the overheads concentration will be in equilibrium with the feed. As the rectifying zone is increased, the overheads concentration will approach the azeotropic concentration.

One of the first decisions in the process of tower design is whether to use a tray or packed column. Tray columns provide staged contact and are more adaptable than packed columns. The operation of tray columns has also been more extensively documented. Tray columns are generally preferred for solutions containing metals, solids, or polymerizable materials. Packed columns provide continuous contact, reducing column height and costs. They are more suited to low pressure operation, especially for corrosive, foaming, or viscous liquids. Packing is also more commonly used if the column diameter is very small.

General Design Equations

Design equations have been previously derived by Hwang and Fahrenthold (1980) and Treybal (1980). Here they are presented with comments relevant to their application.

Design begins with the characterization of the waste itself. For an optimized design, it is necessary to have vapor liquid equilibrium data for the particular waste in question. The relationship between the concentration of the pollutant in the vapor phase and in the liquid phase is often described by the relationship:

$$y = Kx \qquad (1)$$

Here y is the mol fraction of the pollutant in the vapor phase and x the mol fraction in the liquid phase. For economical design, it is always preferred to have equilibrium data available which characterizes the vapor and liquid compositions over the range of operating temperatures. Due to the difficulty of obtaining and generating this data, Henry's Law constants are often used to evaluate the applicability of steam stripping to a particular waste. Shukla and Hicks (1984) have given an ex-

tensive list of equations relating Henry's Law Constants and temperature for a number of organic compounds. Since Henry's Law constants have been reported in so many systems of units, it is always important to use the appropriate correction factors to assure K is dimensionless in the above equation. When Henry's Law constants cannot be found, they can be estimated by the vapor pressure to solubility ratio. If activity coefficients are estimated with UNIFAC (Fredenslund, et. al, 1977), the Henry's Law constant is also approximately equal to the product of the activity coefficient and the vapor pressure of the pollutant.

If the objective of steam stripping is simply to produce a purified effluent, this can be achieved in a packed or staged column without reflux. In order to determine the number of theoretical stages required in a staged column, the following equation may be used:

$$N = \frac{\ln [(x_f/x_b)(S - 1) + 1]}{\ln S} - 1 \qquad (2)$$

Correlations between theoretical plates and actual stages based on the Murphree stage efficiency have been presented by McCabe, Smith, and Harriot (1985). For packed columns without reflux, Montgomery (1985) presented the following equation to determine the required number of transfer units:

$$NTU = \frac{S}{S - 1} \ln \frac{x_f/x_b(S - 1) + 1}{S} \qquad (3)$$

A graphical solution to this problem has been presented by Montgomery (1985). Having solved for the number of transfer units, the correlations presented by Bolles and Fair (1982) can be used to determine the actual height of a particular packing which will be required to make the separation.

When the overheads from a stripper is designated for recovery and high purity is required, reflux becomes necessary. It should be noted that the stripping factor for a column with reflux must take into account the additional liquid being returned to the column. In other words, L (sum of feed rate and returned reflux rate) will increase in a column with reflux. If the treated bottoms concentration must meet a specified limit, in addition to producing a high purity organic overheads, these more rigorous demands on the column will lead to increased column height. The following set of equations (Hwang and Fahrenthold, 1980) may be used to determine the number of theoretical plates required in a staged column with reflux:

$$N = \ln \left[\frac{S(x_b/x_f) + K' + K'S}{x_b/x_f} \right] / \ln S - 1 \qquad (4)$$

$$K' = \frac{1}{R' + 1} (1 + R'\gamma_D/\gamma_S) \qquad (5)$$

$$R' = R\left[1 + \frac{C_p(t_b - t_R)}{\lambda} \right] \qquad (6)$$

Once again, the actual number of trays required should be calculated using the Murphree tray efficiency or some equivalent scheme. The required number of transfer units for a packed bed with reflux can be determined with the following equation(Hwang and Fahrenthold, 1980):

$$NTU = \frac{S}{S-1} \ln\left[x_f / x_b K' \frac{S-1}{S} + 1 + K' \frac{1-S}{S}\right] \qquad (7)$$

The actual height required can be determined using the previously noted correlations of Bolles and Fair (1982). Sizing columns with rectification requires the complete vapor-liquid equilibrium curve and is frequently determined using the graphical methods presented in McCabe, Smith, and Harriot (1985).

After the packing height, or number of trays required for a specified separation has been determined, the sizing of auxilliary equipment can be carried out. Selection of steam and feed flow rates should be evaluated to avoid flooding or weeping conditions (McCabe and Smith, 1985). Generally, steam flow rates are between 10 and 30% of the molar feed rate. A heat exchanger is commonly used to preheat the feed to its bubble point in order to increase column efficiency. Heat exchangers may also be used to cool the bottoms or organic overheads. Care must also be taken in sizing the condenser to assure the collection of the concentrated organics. The condenser vent lines may also require specialized equipment for the removal of organic vapors.

Steam Stripping Research

A pilot-scale steam stripping (Figure 1) unit has been assembled at the EPA Test and Evaluation Facility for assessing the treatability of various organic wastes. This system employs a modular column design, enabling operation with 20, 15, or 10 transfer units. When desired, rectification can also be used to increase the overheads concentration. According to the projections of Hwang and Fahrenthold (1980), a modular column providing up to 20 transfer units should be able to handle any application for which steam stripping would be considered economically feasible. The unit is currently undergoing shakedown with toluene. A preliminary run, to investigate the potential for stripping 2-nitropropane, has been conducted. Various biological and inorganic treatment systems currently in operation at this facility enable the evaluation of treatment train options for complex waste mixtures. A number of solvent containing wastes are candidates for further study.

In addition to the pilot-scale experimentation, computer assisted design methods and steam stripper simulation programs are being written and evaluated. By developing computerized methods to carry out the stage and packing height determinations, prospective designs can be rapidly reviewed. A more rigorous steam stripper simulation program has been described by Henley and Seader (1981). This program is suitable for optimizing the operation of an existing stripping column, or as an aid in evaluating proposed designs.

Continuing work at the Test and Evaluation Facility will involve screening wastes for steam stripper treatability and developing thorough computer assisted design methods. Future work may also include the generation of vapor-liquid equilibrium data and the generation of a database for computerized design methods. The program CHEMEST, which contains an algorithm for UNIFAC calculations, has been purchased for the estimation of vapor-liquid equilibrium constants. Future work will therefore combine pilot-scale runs of various wastes with associated computer design and optimization.

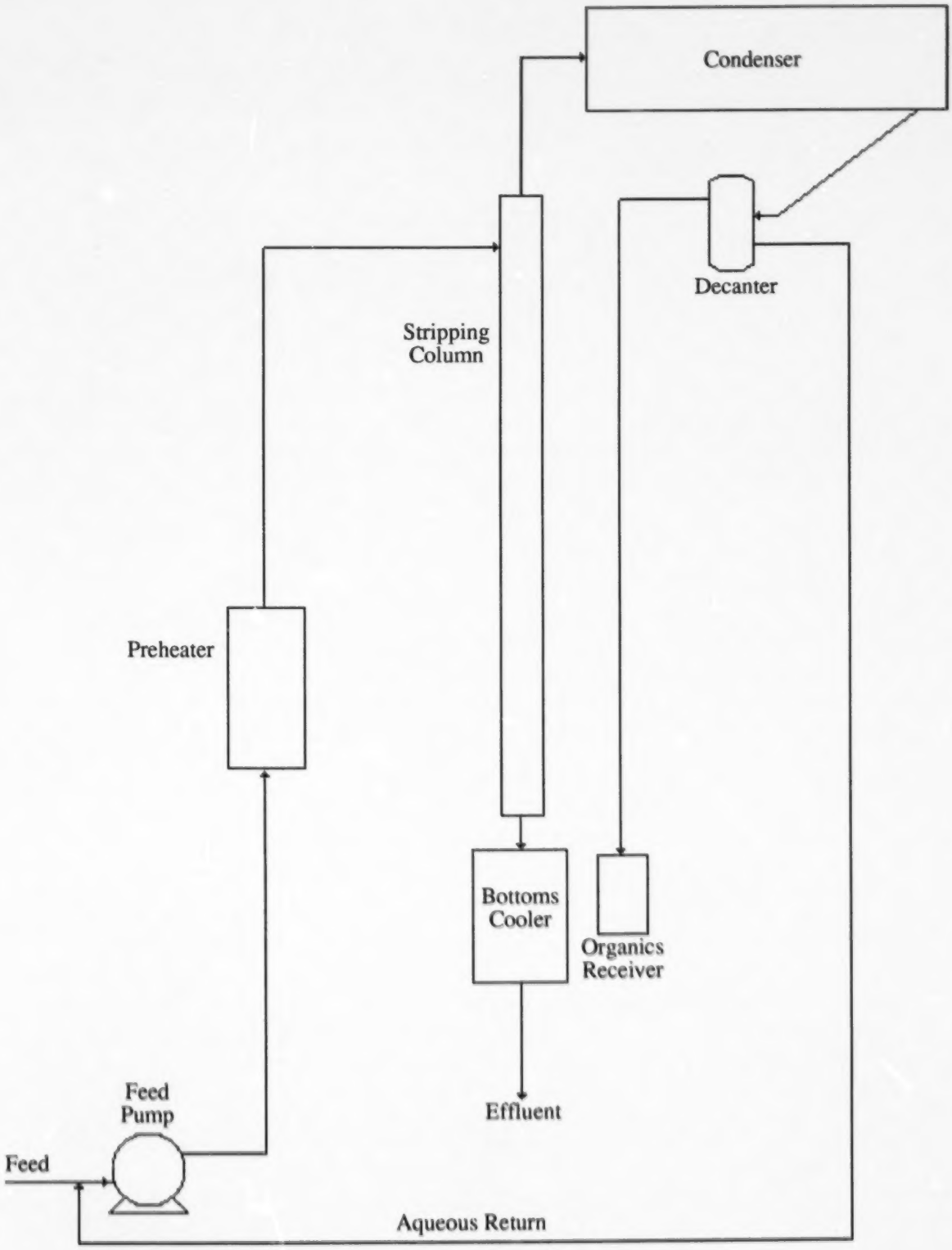

Figure 1
Steam Stripping System

Steam Stripping 2-Nitropropane

2-nitropropane, a nitroparaffin, is a widely used solvent, especially in the coatings industry. Separation processes sometimes use 2-nitropropane as a processing solvent as well. It has also been used in the synthesis of nitro alcohols, amines, and pharmaceutical products. Rocket fuel propellants and explosives may also include 2-nitropropane.

As a result of RCRA, 2-nitropropane has been classified as a component of F005 and has itself been assigned the Hazardous Waste Number U171 (40 CFR, Part 261, Appendix VIII). In general, nitroparaffins can be classified as moderately toxic. At very high concentrations, inhalation of 2-nitropropane can produce fatal methemoglobinemia. Much of the interest in 2-nitropropane, however, stems from its potential carcinogenicity (Lewis, et. al., 1979).

The reactive and flammable nature of 2-nitropropane, as well as its potential carcinogenicity, warrant considerable safeguards in handling and disposal. 2-Nitropropane was listed by ammendment to RCRA in CFR 40 during 1986. This listing applied to spent solvents (ranging in concentration from 50 to 95%) and still bottoms (ranging from 1 to 20%). Due to its high mobility, EPA considers this compound to pose a significant threat to groundwater. The purpose of this study was to assess the feasibility of treating dilute aqueous solutions of 2-nitropropane with steam stripping.

A comparison of the physical properties of 2-nitropropane with the criteria for steam stripping produces mixed results. The solubility of 2-nitropropane at 25°C is 1.7%, considerably higher than the ideal candidate for steam stripping. Running without rectification can not produce both aqueous and organic layers in the decanter. Nevertheless, 2-nitropropane does form a low boiling aqueous azeotrope (bp 88.55°C) and has a modestly favorable Henry's Law constant at 100°C (estimated using UNIFAC at 1.7×10^{-3} atm-m^3/mol).

In order to assess the applicability of steam stripping to 2-nitropropane containing wastes, the pilot-scale steam stripping column was run in the 20 theoretical plate mode with total recycle (comparable to reflux) to minimize the volume of the concentrated overheads product. Without rectification, no organic layer developed in the decanter. Samples were collected at 30 minute intervals using glove boxes on the feed, bottoms, and overheads lines. The analytical results are presented in Table 1.

Table 1

Average Concentration (mg/L)		
Feed	Bottoms	Overheads
2,397	0.114	4,630
1,431	0.141	4,480
691	0.456	4,970
934	0.398	4,740
719	0.319	6,550
711	0.348	5,980

Batch Distillation

The operation of a batch still is very similar in principle to a simple laboratory distillation. A liquid charge is placed into the still and heated. The vapor formed is continuously removed and condensed. In this mode of operation, there is no steady state. The composition of both the liquid remaining in the still and the vapor phase are continually changing as the process proceeds. While continuous distillation columns are now common for commercial production of chemicals, batch distillation is more advantageous when processing wastes intermittantly or when treating wastes with variable composition. This flexibility makes batch distillation the method of choice for many solvent recovery operations and is of particular interest to small quantity generators.

A wide variety of solvent wastes can be processed in batch stills, including high solids and explosive mixtures. Stills are commonly operated at 20°F to 30°F higher than the boiling point of the solvent in order to assure vaporization. Systems with high solids (boiling point elevation) or with high boiling azeotropes must be operated at higher temperatures (Breton, et. al., 1986). The temperature of the still should be maintained at least 40°C below the autoignition point in order to prevent explosions. The autoignition point for many solvents can be found in the National Fire Protection Association's "Fire Protection Guide for Hazardous Materials"(1986).

While many small batch distillation units are designed to be explosion-proof, the potential for an explosion when dealing with solvent mixtures should still be evaluated. At high temperatures, thermal decomposition may also occur. This is especially common when working with halogenated solvents. Vacuum operation reduces the required temperature to achieve separation of autoignitable wastes and solvents subject to thermal decomposition (Breton, et. al., 1986).

Batch stills are heated indirectly using coils and jackets filled with hot oil or steam. Temperature is maintained until the time/temperature profile indicates the predetermined fraction of solvent has been removed. After completion, the still residues are removed. Trying to recover excessive amounts of solvent may produce residues which foul heating jackets and coils . These residues are commonly incinerated and therefore the distillation should be discontinued while the residue still has a reasonable Btu value and remains pumpable.

General Design Procedures

Simple batch distillation units are among the most common solvent recovery schemes. These units consist of a heated vessel, a condenser, and a receiver. Unlike units with rectification, there is no column. These popular units are essentially a single theoretical stage. Equations governing the operation of these units for constant or average relative volatility (α) have been presented in Perry and Chilton (1973). In this case, the following equation is solved for the solvent of greatest interest (key component):

$$\ln (W_e/W_i) = \frac{1}{\alpha - 1} \ln \frac{x_e(1 - x_i)}{x_i(1 - x_e)} + \ln \frac{1 - x_i}{1 - x_e} \qquad (8)$$

where W_e is the final number of moles in the still and W_i is the initial number of moles in the charge. The results of this determination can be extended to any other components in the waste by the equation:

$$\ln (W_{A(e)}/W_{A(i)}) = \alpha \ln (W_{B(e)}/W_{B(i)}) \qquad (9)$$

Here, $W_A(e)$ and $W_A(i)$ refer to the final and initial moles of component A and $W_B(e)$ and $W_B(i)$ refer to the final and initial moles of component B in the still.

More difficult separations can be achieved by using rectification. This requires the use of a tray or packed column with the batch still. Due to the changing composition of the liquid in the still, calculation procedures are especially difficult for batch distillation with rectification. The Chemical

Engineers' Handbook by Perry and Chilton (1973) has presented graphical solution methods for the separation of binary mixtures. For batch rectification with constant reflux, a series of operating lines (reflecting changing composition) with equivalent slope must be drawn on the x-y diagram. When using variable reflux to maintain constant overheads composition, a series of operating lines with different slopes must be drawn to produce constant distillate composition. In either case, as the distillation proceeds, the behaviour of the column can be modelled by sequentially utilizing the series of operating lines generated to step of trays in the McCabe Thiele fashion.

Batch Distillation Research

A rectified stillwith 50 theoretical plates (Figure 2) has been assembled at the Test and Evaluation Facility. This packed column is currently undergoing wet testing and will be used for solvent recovery assessment studies. Future work may explore the utility of batch distillation as part of a treatment train including steam stripping, inorganics treatment, or biological polishing. All results will be compared with the graphical methods for constant reflux (Perry and Chilton,1973). Future work may also include the use of a process gas chromatograph to maintain constant distillate composition. A computer algorithem for simple batch stills will be developed. Programs which would aid in the design or simulation of rectified batch distillation are also being considered.

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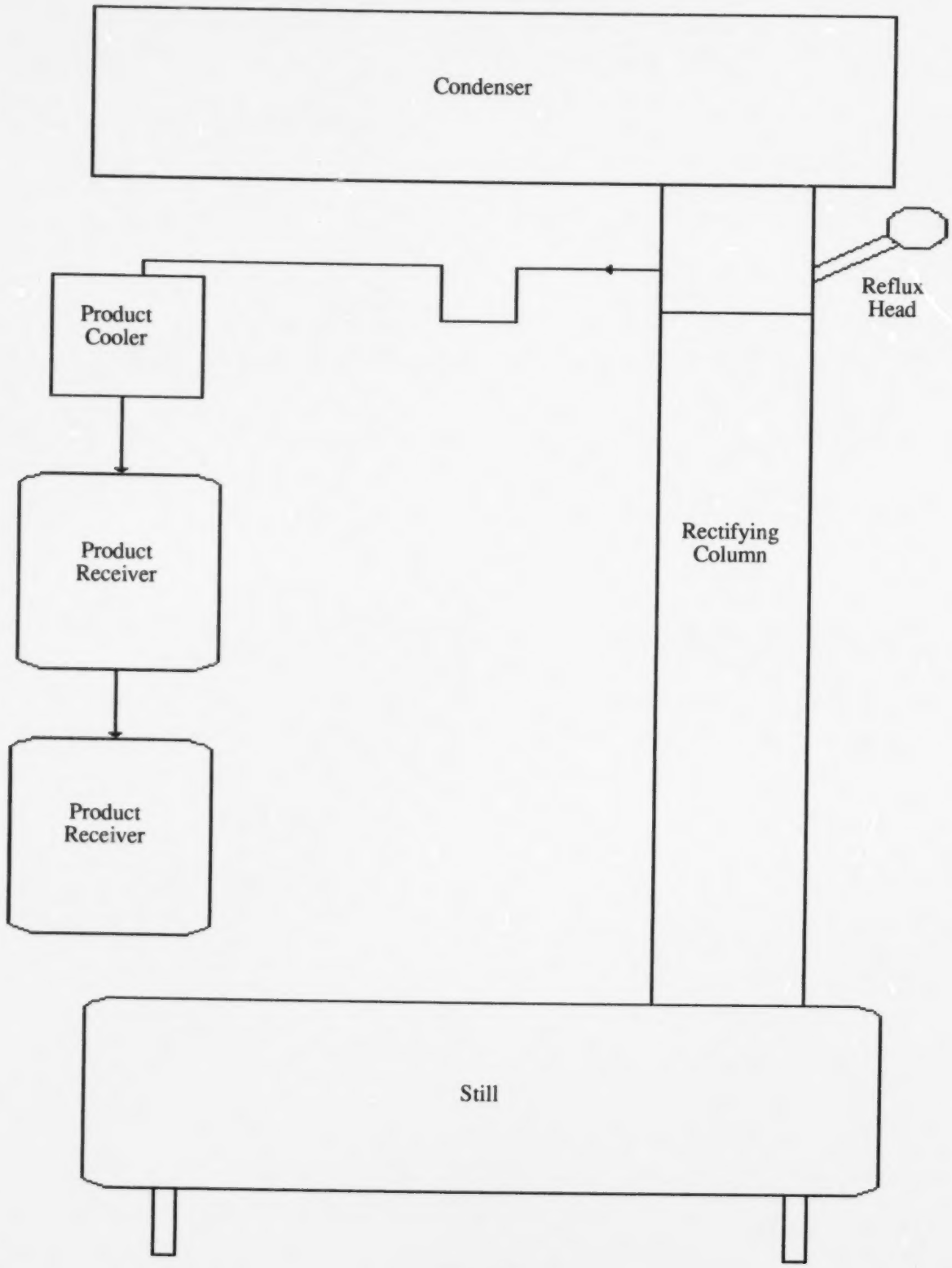

Figure 2
Batch Distillation Unit

List of Abbreviations

NOTATION

C_p - specific heat of reflux
K^p- vapor-liquid equilibrium constant
K'- intermediate variable (defined by eqn. 5)
L - liquid flow (lbmol/hr)
N - number of theoretical stages in a tray column
NTU - number of transfer units in a packed column
R - reflux ratio
R'- intermediate variable (defined by eqn. 6)
S - stripping factor (S = KV/L)
V - vapor flow (lbmol/hr)
W_A(e)-final number of mols of component A in the still
W_A(i)-initial number of mols of component A in the still
t_b - boiling point of aqueous reflux
t_R - reflux temperature
x - mol fraction of the pollutant in the liquid phase
x_b - mol fraction of the pollutant in the effluent (bottoms)
x_e - mol fraction of the pollutant in the still residue
x_f - mol fraction of the pollutant in the feed
y - mol fraction of the pollutant in the vapor phase

GREEK LETTERS

α - relative volatility (as defined by the ratio of K values for two components)
γ_D - activity coefficient of the organic phase
γ_S - activity coefficient of the aqueous phase
λ - latent heat of steam

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